isomer VII, was resistant to the action of alkaline permanganate in water (96% recovery).

Reductive Acylation of XIII.—A mixture containing compound XIII (849 mg., 2.71 mmoles), acetic acid (25 ml.), acetic anhydride (12 ml.), Raney nickel (one teaspoon) and hydrogen (39 p.s.i.), was shaken for 15 minutes at 25°. The resulting mixture was filtered (solid washed with acetic acid) and the filtrate was diluted with water (100 ml.). The white solid that separated was collected, washed with water and recrystallized from 95% ethanol. 2,4-Diphenyl-5-acetylaminothiophene (XIV) (m.p. and mixed m.p. 162–163°) was obtained in 41% yield (324 mg.). This material caused no depression in melting point when admixed with authentic XIII.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Conjugative Effects in Divalent Sulfur Groupings[1]

BY F. G. BORDWELL AND PIERRE J. BOUTAN[2]

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From measurements of the acidity constants of *m*- and *p*-substituted benzoic acids and phenols it is concluded that the order of electron-pair donor type conjugation is $(CH_3)_2N > CH_3O > CH_3S$, and $CH_3CONH > CH_3COO > CH_3COS$. This order also expresses the relative activating influence of the groups in aromatic substitution. Acidity constant and ultraviolet absorption spectral measurements indicate that electron-pair acceptor conjugation for SH, SCH_3, $SCOCH_3$ and SCN groups with groups like *p*-OCH_3 or *p*-O^- is slight. It is concluded that the presence of a powerful electron-donor, such as a carbanion, is necessary to evoke a clearly recognizable electron pair acceptor type conjugation in divalent sulfur groups.

It seemed desirable to extend the acidity constant method, which has revealed electron-pair acceptor conjugative effects for sulfone,[3] sulfonium,[4] sulfoxide[5] and sulfonate[6] groups, to groups containing divalent sulfur. The present paper reports such a study and includes some related work on ultraviolet absorption spectra and aromatic substitution reactions.

Electron-pair Releasing Conjugative Effects. Acidity Constant Measurements.—Evidence for the relative ability of CH_3S, CH_3O and $(CH_3)_2N$ groups to release electrons in conjugative interactions with the carboxyl groups was obtained by examining the acidity constants of *m*- and *p*-substituted benzoic acids and phenols. The electronic effects of the groups may be expressed as Hammett sigma (σ) constants.[7] Since conjugative interactions should be absent between *meta* groups, and since differences in inductive effects between *meta* and *para* positions are small, the differences $\sigma_{para} - \sigma_{meta}$ of benzoic acids gives an approximate measure of conjugative effects. These groups should not conjugate with the hydroxyl group in phenols, so differences between the σ_{para}-constants of substituted benzoic acids and phenols should also be a rough measure of conjugation in the benzoic acids. Pertinent data have been compiled in Table I.

TABLE I

HAMMETT σ-CONSTANTS CALCULATED FROM ACIDITY CONSTANTS OF *m*- AND *p*-SUBSTITUTED BENZOIC ACIDS AND PHENOLS

	Benzoic acids		Phenols	
Substituents	σ	$\sigma_p - \sigma_m$	σ	$\sigma_p - \sigma_m$
m-$(CH_3)_2N$	−0.16[a]		+0.04[f]	
p-$(CH_3)_2N$	− .72[a]	−0.56	− .12[f]	−0.16
m-H_2N	− .16[b]		+ .03[g]	
p-H_2N	− .66[b]	− .50	− .15[g]	− .18
m-CH_3O	+ .11[b]		+ .13[e]	
p-CH_3O	− .27[b]	− .38	− .11[e]	− .24
m-HO	+ .06[c]		+ .06[g]	
p-HO	− .31[d]	− .37	− .17[g]	− .23
m-CH_3S	+ .14[e]		+ .23[f]	
p-CH_3S	− .01[e]	− .15[h]	+ .21[f]	− .03

[a] C. C. Price and D. C. Lincoln, THIS JOURNAL, **73**, 5838 (1951). [b] Ref. 7. [c] J. D. Roberts and W. T. Moreland, THIS JOURNAL, **75**, 2267 (1953). [d] J. F. G. Dippy, *Chem. Revs.*, **25**, 207 (1939). [e] Ref. 3a. [f] Present investigation, see Experimental section. [g] A. Kuhn and A. Wasserman, *Helv. Chim. Acta*, **11**, 23 (1928). [h] This difference agrees well with the difference of −0.17 obtained by C. C. Price and J. J. Hydock, THIS JOURNAL, **74**, 1945 (1952), from the saponification of substituted ethyl benzoates.

The greater the $\sigma_p - \sigma_m$ difference for benzoic acids, the higher is the order of conjugative ability of the electron-releasing group with the carboxyl group. From Table I the order is seen to be $(CH_3)_2N = H_2N > CH_3O = HO > CH_3S$. This is the order predicted by Ingold[8] and that found by Baker, Barrett and Tweed[9] using a method different from that of the present investigation.

Since conjugative effects are not expected in the phenols the $\sigma_p - \sigma_m$ differences here should be constant. Table I reveals that this is true for the most part, only the difference for the CH_3S group being out of line.

The σ_{meta}-constants for a given group should be the same whether determined from benzoic acids or phenols if the interactions are purely inductive. This is true for *m*-CH_3O and *m*-HO groups and the difference for *m*-CH_3S is not much greater than the experimental error. The differences for *m*-H_2N and *m*-$(CH_3)_2N$ appear to be definitely outside of experimental error, however, and suggest a disturb-

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(1) This investigation was supported in part by the American Petroleum Institute as part of Project 48B.

(2) Texas Company Research Fellow 1952–1954.

(3) (a) F. G. Bordwell and G. C. Cooper, THIS JOURNAL, **74**, 1058 (1952); (b) F. G. Bordwell and H. M. Andersen, *ibid.*, **75**, 6019 (1953); (c) H. J. Backer and H. Kloosterziel, *Rec. trav. chim.*, **71**, 295 (1952).

(4) F. G. Bordwell and P. J. Boutan, THIS JOURNAL, **78**, 87 (1956).

(5) F. G. Bordwell and P. J. Boutan, Abstracts of papers presented at the Chicago Meeting of the American Chemical Society, Sept. 6–11, 1953, p. 80-O.

(6) H. Zollinger, *Nature*, **172**, 257 (1953).

(7) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapter VII.

(8) C. K. Ingold and E. A. Ingold, *J. Chem. Soc.*, 1310 (1926); E. K. Holmes and C. K. Ingold, *ibid.*, 1328 (1926).

(9) J. W. Baker, C. F. Barrett and W. T. Tweed, *ibid.*, 2831 (1952).

ance from a field effect or an unusual type of conjugation.[10]

Comparison of the increase in σ_{para}-constants in going from phenols to benzoic acids can also be taken as a measure of conjugation, assuming the absence of conjugation in the phenol. For *p*-$(CH_3)_2N$, *p*-H_2N, *p*-CH_3O, *p*-HO and *p*-CH_3S groups the increase is 0.60, 0.51, 0.16, 0.14 and 0.22 σ-unit, respectively. This suggests the order $(CH_3)_2N = H_2N > CH_3S > CH_3O = HO$, although the difference between the CH_3S and CH_3O or HO group is not large and may not be significant. It is possible that the discrepancy with the CH_3S group may arise from an electron-acceptor conjugation effect for the *p*-CH_3S group (see later discussion).

The ability of the *para* groups to decrease the acidity of benzoic acid is another way to represent the conjugative effects of electron-releasing groups. From a consideration of electronegativities[11] of oxygen, nitrogen and sulfur, the groups should be acid strengthening in the order *p*-$CH_3O > (CH_3)_2N > CH_3S$. Actually, as indicated by their σ-constants, the groups are acid weakening in the order *p*-$(CH_3)_2N$ (σ −0.72) > *p*-CH_3O (σ −0.27) > *p*-CH_3S (σ −0.01). Ingold first suggested a conjugative effect to account for data of this type.[12]

The lesser ability of CH_3S as compared to CH_3O in electron-releasing conjugative interactions may occasion some surprise in view of the high nucleophilicity associated with divalent sulfur when initiating displacement reactions.[13] The latter is, however, a polarizability effect generated at the demand of the reagent at the instant of reaction. The acidity constant approach measures an equilibrium-type electron-releasinga bility, and sulfur is apparently much less capable of supplying electrons in this type of interaction. The situation is analogous to the order of conjugative ability F > Cl > Br > I for halogens as compared to the order I > Br > Cl > F for the nucleophilicity of their ions. This order of conjugative effects bears out the early conclusion of Lewis that second row elements have less tendency than first row elements to form double bonds.[14]

Extension of the study to $\sigma_p - \sigma_m$ values for CH_3CONH, CH_3COO and CH_3COS groups from the measurements of acidity constants of benzoic acids led to the results summarized in Table II. The data show the order of effective conjugation of the groups with a *p*-carboxyl group to be $CH_3CONH > CH_3COO > CH_3COS$, in agreement with the order $(CH_3)_2N > CH_3O > CH_3S$.

TABLE II

APPARENT IONIZATION CONSTANTS OF *m*- AND *p*-SUBSTITUTED BENZOIC ACIDS IN 50% ALCOHOL

Substituents	pK_a	σ	$\sigma_p - \sigma_m$
H	5.71	....	....
m-CH_3CONH	5.35	+0.25	
p-CH_3CONH	5.68	+ .02[a]	−0.23
m-CH_3COO	5.16	+ .38[b]	
p-CH_3COO	5.29	+ .29	− .09
m-CH_3COS	5.17	+ .37	
p-CH_3COS	5.09	+ .42	+ .05

[a] H. H. Jaffé, L. D. Freedman and G. O. Doak, THIS JOURNAL, **75**, 2209 (1953), give σ-values of −0.01, −0.02 and −0.10, and H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953), gives a value of −0.015. [b] This value checks satisfactorily the value of +0.32 calculated from the pK_a value of 3.88 in water at 25° found by L. O. Smith and H. C. Jones, *Am. Chem. J.*, **50**, 31 (1913), using a conductivity measurement. It does not check well with the $\sigma_{m\text{-}CH_3COO}$ of +0.19 calculated from the data of W. Ostwald, *Z. physik. Chem.*, **3**, 241 (1889). The σ-constants calculated from Ostwald's conductivity measurements, which were carried out in water, are −0.18, +0.13 and −0.09 for *p*-CH_3COO, *m*-CH_3CONH and *p*-CH_3CONH, respectively. These also fail to agree well with the present values. Some of Ostwald's values for acidity constants check very well with those currently accepted while others do not [see J. F. G. Dippy, *Chem. Revs.*, **25**, 207 (1939)]. We were not able to use water for our determinations because of the low solubility of these compounds.

Aromatic Substitution.—According to current theory both activation of the benzene nucleus by ortho-para directing groups, and orienting effects, are associated with resonance stabilization of the intermediate complex, which is determined by the conjugative ability of the orienting group.[15] It is of interest to note that the order of activating effect in aromatic substitution appears to parallel that of conjugative ability as interpreted from the acidity constant measurements, namely, $(CH_3)_2N > CH_3O > CH_3S$, and $CH_3CONH > CH_3COO > CH_3COS$.[15] Not many data are available regarding the orienting ability of the CH_3S group, but, judging from the fact that bromination of *p*-$C_2H_5OC_6H_4SCH_3$ and *p*-$CH_3C_6H_4SCH_3$ occurs *ortho* to the C_2H_5O group[16a] and CH_3 group,[16b] it appears to have much less activating ability than $(CH_3)_2N$ or CH_3O.

The fairly large positive σ-constant (+0.25) obtained for *m*-$CH_3CONHC_6H_4COOH$ shows that the CH_3CONH group is electron withdrawing when not conjugated with a strong electron-accepting group. Even when conjugated with COOH, as in *p*-$CH_3CONHC_6H_4COOH$, the CH_3CONH group is not electron releasing. It seemed, therefore, worthwhile to test its activating influence by a competitive nitration experiment.[15] Nitration of a mixture of one mole of acetanilide and one mole of benzene with one mole of nitric acid in the presence of sulfuric acid under conditions which have been used for nitration of acetanilide,[17] gave mostly nitrobenzene. Competitive nitration with nitric acid and acetic acid gave mostly *p*-nitroacetanilide, and competitive bromination gave mostly *p*-bromoacetanilide. Evidently the CH_3CONH group is activating toward substitution, but in the presence of

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(10) J. D. Roberts and W. T. Moreland, THIS JOURNAL, **75**, 2167 (1953), have shown that field effects may be of considerable importance in *m*- and *p*-substituted aromatic compounds.

(11) L. H. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1948, p. 60.

(12) C. K. Ingold, *J. Chem. Soc.*, 1124 (1933).

(13) For example, O. R. Quayle and E. E. Royals, THIS JOURNAL, **64**, 226 (1942), found the thiophenoxide ion to be about 1000 times as reactive in displacing the bromine of butyl bromide as is the phenoxide ion.

(14) G. N. Lewis, "Valence and the Structure of Atoms and Molecules," The Chemical Catalog Co. (Reinhold Publ. Corp.), New York, N. Y., 1923, p. 94.

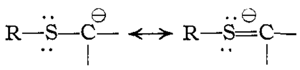
(15) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter VI, on Electrophilic Aromatic Substitution.

(16) (a) T. Van Hone, *Bull. acad. belg.*, [5], **37**, 98 (1928); (b) Th. Zincke and W. Frohneberg, *Ber.*, **43**, 837 (1909).

(17) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1941.

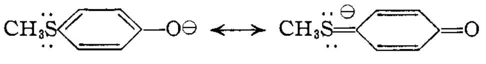
sulfuric acid the formation of $CH_3CO\overset{+}{N}H_2C_6H_5$ is extensive enough to prevent it from exerting its usual activating influence. The activating effect of the CH_3CONH, despite its positive σ-constants, can be rationalized, since it can no doubt exert a stronger conjugating influence when interlocked with the positive charge of the substitution intermediate than with the carboxyl group.

Electron-pair Accepting Conjugative Effects. Acidity Constants.—Evidence has been forthcoming from a number of different experiments to indicate that an α-hydrogen atom in substituted sulfides is more acidic than a similarly situated hydrogen atom in ethers. The data include: (1) ease of elimination of a β-grouping,[18] (2) selectivity in the direction of base-catalyzed ring closure,[19] (3) ease of prototropic shift from allyl to propenyl sulfides,[20] and (4) side chain rather than ring metallation of methyl phenyl sulfide with sodium and lithium reagents.[21] The acidity of the α-hydrogen in these sulfides generally has been attributed to the ability of sulfur to accept electrons in a conjugative effect, thereby expanding its valence shell to ten electrons

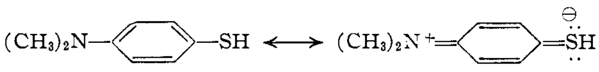


$$R-\underset{..}{\overset{..}{S}}-\overset{\ominus}{C}- \longleftrightarrow R-\underset{..}{\overset{..\ominus}{S}}=C-$$

In a previous section it was pointed out that $\sigma_p - \sigma_m$ for the CH_3S group in phenols is unexpectedly small, and that the difference in $\sigma_{p\text{-}CH_3S}$ for benzoic acids and phenols is greater than the difference for $\sigma_{p\text{-}CH_3O}$. A possible explanation for these somewhat anomalous results could conceivably lie in an unexpectedly high positive value for $\sigma_{p\text{-}CH_3S}$ in phenols caused by an electron-pair acceptor type resonance. This type of resonance would be acid strengthening, and would tend to increase the positive values of $\sigma_{p\text{-}CH_3S}$.



If this type of conjugation is possible for divalent sulfur it might lead to conjugation between p-$(CH_3)_2N$ or CH_3O groups and SH. Conjugation of this nature would be less effective, however, due to



the separation of charge required. It should lead to a decreased acidity [more negative σ-value for p-$(CH_3)_2N$] for such thiophenols compared to that expected, since this conjugation would be more effective in the undissociated form of the thiophenol. This effect should be absent in phenols and inoperative between *meta* positions. Therefore, the $\sigma_p - \sigma_m$ differences should be greater in thiophenols than in phenols. Examination of Table III shows that this is not true. The inconstancy of the σ_m-constants for the $(CH_3)_2N$ group is somewhat disturbing. It seems possible that this may be due to differential solvent effects or a field effect.[10]

TABLE III

ACIDITY CONSTANT AND σ-VALUES FOR PHENOLS AND THIOPHENOLS CONTAINING $(CH_3)_2N$ AND CH_3O SUBSTITUENTS

	Phenols (in H_2O)			Thiophenols (in 48% EtOH)		
Substituent	pK_a	σ	$\sigma p - \sigma m$	pK_a	σ	$\sigma p - \sigma m$
m-CH_3O–	9.65[a]	+0.13		7.54[b]	+0.06	
p-CH_3O–	10.20[a]	– .11	–0.24	8.08[b]	– .15	–0.21
m-$(CH_3)_2N$–	9.85	+ .04		7.94	– .09	
p-$(CH_3)_2N$–	10.22	– .12	–0.16	8.37	– .26	–0.17

[a] Ref. 3a. [b] G. Swarzenbach and E. Rudin, *Helv. Chim. Acta.*, 22, 360 (1939).

It is well established that sulfonyl,[3] sulfinyl,[5] sulfonium[4] and sulfonate[6] groups can enter into electron-acceptor type conjugation. It seemed likely, then, that if the sulfur atom could be made more positive in the divalent sulfur group this type of conjugation should become more pronounced. We, therefore, undertook the measurement of some acidity constants for phenols and benzoic acids containing the CH_3COS and SCN groupings. Electron-pair acceptor conjugation in the phenol, such as is shown for p-$NCSC_6H_4O^-$, should be enhanced with these groups. Electron-pair donor conjugation in the benzoic acid, if it occurs, would serve to exaggerate the difference in σ_p-constants between benzoic acids and phenols.

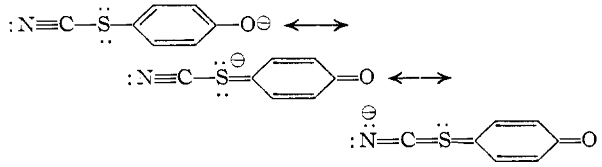


TABLE IV

σ-CONSTANTS FOR p-$SCOCH_3$ AND p-SCN GROUPS

Substituent	Benzoic acids pK	σ	Phenols pK	σ
p-CH_3COS	5.09	+0.42	8.88	+0.46
p-SCN	4.97	+ .51	8.57	+ .60

The data summarized in Table IV show that σ_p-constants for the CH_3COS group are the same, within experimental error, in phenols as in benzoic acids. There is no evidence for conjugation.

The 0.09 higher value for σ_{p-SCN} for phenols than for benzoic acids may be ascribed to a small conjugative effect of this kind, but this difference is not far outside the experimental error.

Campbell and Rogers[22] have suggested a resonance interaction in p-$(CH_3)_2NC_6H_4SCN$ and p-$H_2NC_6H_4SCN$ on the basis of dipole moment measurements and calculations. Conjugation should be greater in the anilines, and a small effect would produce a relatively large change in the dipole moment in these molecules, since the charge separation is great, so their data are not necessarily incompatible with ours.

The results with the CH_3COS and SCN groups are reminiscent of the study of the rates of hydrolysis of aryl chloromethyl sulfides, $ArSCH_2Cl$, which showed that σ_{p-CH_3O} for this reaction is about that

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(18) E. Rothstein, *J. Chem. Soc.*, 1556, 1558 (1940).

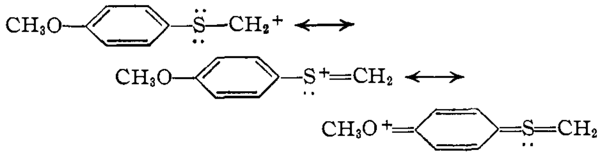
(19) (a) R. B. Woodward and R. H. Eastman, THIS JOURNAL, **68**, 2229 (1946); (b) W. J. Brehm and T. Levenson, *ibid.*, **76**, 5389 (1954).

(20) D. S. Tarbell and M. A. McCall, *ibid.*, **74**, 48 (1952).

(21) H. G. Gilman and F. J. Webb, *ibid.*, **71**, 4062 (1949). Note, however, that metallation with magnesium or less active metals gives nuclear metallation, and higher alkyl phenyl sulfides give nuclear metallation with all reagents.

(22) T. W. Campbell and M. T. Rogers, THIS JOURNAL, **70**, 1029 (1948).

calculated for benzoic acid.[23] The evidence suggested no more than a small resonance interaction between the methoxyl group and the sulfur grouping of the type shown.



Aromatic Substitution.—The exclusive *ortho–para* orienting effect of the SCN group[24] is remarkable in view of the large electron-withdrawing effect indicated by the relatively large positive σ-value (+0.51). For comparison note that the *meta*-directing CH_3CO group has an identical σ-value.[3a] The strong deactivating effect of the SCN group was confirmed by carrying out a nitration of a mixture of equal molar quantities of benzene and thiocyanobenzene with one-half the theoretical quantity of nitrating agent. Nitrobenzene was the only isolable product.

The SCN group belongs in the category of groups which deactivate the nucleus, but direct *ortho–para* due to the ability of the unshared pairs of electrons on the atom attached to the ring to enter into conjugation in the transition state or intermediate complex formed in the aromatic substitution reaction. Judging from its σ_p-constant, the SCN group is probably the most strongly electron-withdrawing of these groups, which include the halogens, $CH{=}CHCOOH$ and $CH{=}CHNO_2$ groups.[25]

Ultraviolet Absorption Spectra.—Fehnel and Carmack[26a] and also Koch[26b] have shown that conjugative interaction of the RS with C_6H_5 or $CH{=}CH$ groups results in a large bathochromic shift in the ultraviolet absorption spectrum. Since this shift is greatly enhanced by the introduction of p-NO_2 and similar groups in phenyl sulfides, but remains almost unchanged by the introduction of a p-HO group, it seems to be best interpreted as an electron-pair donor type of conjugative effect for sulfur. Both Fehnel and Carmack[26a] and Koch[26b] admit the possibility of electron-acceptor type conjugation for sulfur, but in our opinion the evidence presented for such an effect is slight.

Recently it has been suggested[27] that the change in the spectrum of phenyl thiolacetate from that of a broad maximum in the 230–240 mμ region to a sharp maximum of higher intensity in this same region resulting from substitution of a methoxyl group in the *para* position "almost certainly indicates that the sulfur atom participates in the electronic transition corresponding to this band by using a 3d orbital." Cilento believes[27a] that the sulfur in aryl thiolesters can act "equally well as a donor or acceptor."

The effect of introduction of a p-hydroxyl group on the spectrum of phenyl thiolacetate is similar to that observed by Cilento[27] for the introduction of a p-methoxyl group (Fig. 1). The spectra for C_6H_5SCN and p-HOC_6H_4SCN show similar changes, but here a sharp maximum is present for *each* of these compounds (Fig. 2) with a shift of 6 mμ to longer

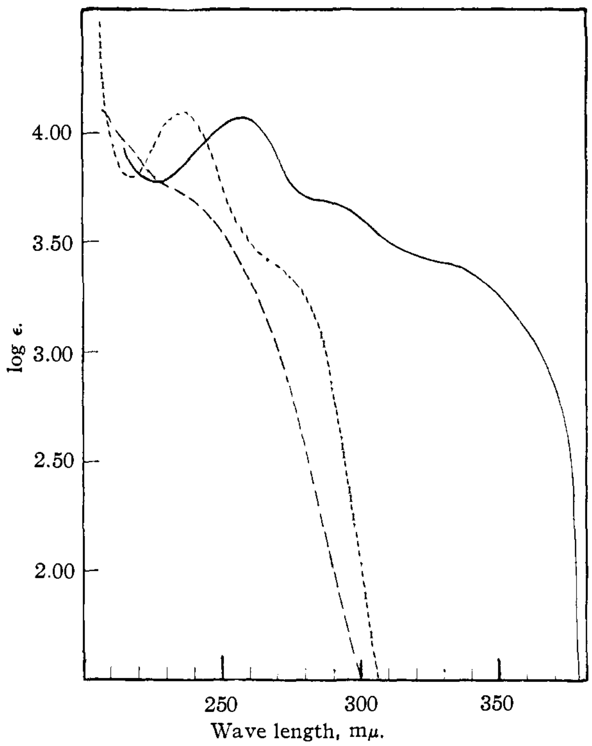


Fig. 1.—Ultraviolet absorption spectra measured in water at 28° for: $C_6H_5SCOCH_3$, - - -; p-$CH_3COSC_6H_4OH$, ------; and p-$CH_3COSC_6H_4O^-$, ——.

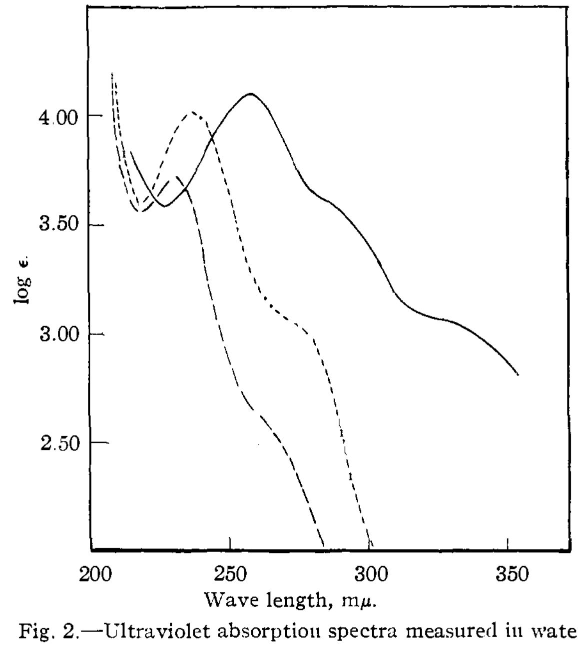


Fig. 2.—Ultraviolet absorption spectra measured in water at 28° for: C_6H_5SCN, - - -; p-$NCSC_6H_4OH$, ------; and p-$NCSC_6H_4O^-$, ——.

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(23) F. G. Bordwell, H. M. Andersen, H. Morita, B. M. Pitt and G. D. Cooper, Abstracts of papers presented at the American Chemical Society Meeting in Atlantic City, N. J., Sept. 14–19, 1952, p. 5M.

(24) F. Challenger and A. D. Collins, *J. Chem. Soc.*, **125**, 1327 (1924).

(25) F. G. Bordwell and K. Rohde, THIS JOURNAL, **70**, 1191 (1948).

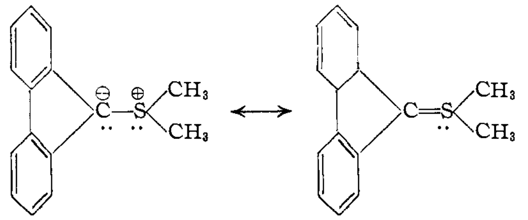
(26) (a) E. A. Fehnel and M. Carmack, *ibid.*, **71**, 84, 231, 2889 (1949); (b) H. P. Koch, *J. Chem. Soc.*, 387 (1949).

(27) (a) G. Cilento, THIS JOURNAL, **75**, 3748 (1953); (b) G. Cilento and W. F. Walter, *ibid.*, **76**, 4469 (1954).

wave lengths for the hydroxy compounds. Shifts of this order of magnitude do not indicate a significant conjugative effect. In view of the results with the thiocyano compounds, it seems likely that the broad absorption maximum present in $C_6H_5SCOCH_3$ is merely resolved in p-$CH_3OC_6H_4SCOCH_3$ and p-$HOC_6H_4SCOCH_3$ into a band with a narrower maximum and a shoulder (see Fig. 1). If conjugation is correlated with shifts in the positions of band maxima rather than changes in intensity of absorption, which appears to be more profitable,[28] these spectra do not provide evidence for electron-acceptor conjugation. This view is strengthened by the observation that the maximum for each of the phenols, p-$HOC_6H_4SCOCH_3$ and p-HOC_6H_4SCN, is shifted by 21 mμ on converting them to the phenolate ion. This corresponds to the 24.5 mμ difference between phenol itself and the phenolate ion.[28] It does not agree with the behavior of a conjugated phenol, such as p-$CH_3COC_6H_4OH$, where the shift is 49.5 mμ.[28] In our opinion the spectral evidence offers no support for electron-acceptor type conjugation for the thiolester group.

Conclusion

Our general conclusion from the acidity constant and spectral measurements is that electron-pair acceptor type of conjugation for sulfur in divalent sulfur groups is usually small or negligible. Conjugation of this type will be largest with strong electron-donor groups, so the small effects of this type seeming to operate between $-O^-$ and CH_3S or SCN groups may be real, although they are not far outside of experimental error. Apparently it is necessary to have an electron-pair donor of the strength of a carbanion[18-22] in order to evoke a clearly recognizable effect. Even in such instances the effect may not be large, as indicated by the conclusion of Ingold[29] that the remarkable compound prepared by Ingold and Jessop[29] is primarily dipolar in type.



Experimental[30]

Preparation of Materials.—The compounds used were for the most part obtained by procedures given in the literature. The preparation of *m*- and *p*-dimethylaminophenol and *m*- and *p*-dimethylaminothiophenol has been described previously.[4] In a few instances new synthetic routes were used and these are given below.

m-Acetylthiobenzoic Acid.—Fifty grams of ice followed by 5.0 g. (0.05 mole) of acetic anhydride were added to an ice-cold solution of 6.16 g. (0.04 mole) of *m*-mercaptobenzoic acid, 5.6 g. (0.10 g.) of potassium hydroxide and 56 ml. of water. The resulting mixture was shaken 15 minutes, acidified and the material which precipitated out filtered and washed with water. Recrystallization of this crude product from benzene–hexane gave 5.0 g. (64%) of a hard crystalline material, m.p. 152–153°.

Anal. Calcd. for $C_9H_8O_3S$: C, 55.09; H, 4.11; neut. equiv., 196.2. Found: C, 55.54; H, 4.26; neut. equiv., 190.9.

p-Acetylthiobenzoic Acid.—Acylation of *p*-mercaptobenzoic acid by the above method gave 60% of a material, m.p. 188–190°. Recrystallizations from chloroform–benzene raised the melting point to 202.5–203.5°.

Anal. Calcd. for $C_9H_8O_3S$: C, 55.09; H, 4.11; neut. equiv., 196.2. Found: C, 55.31; H, 4.21; neut. equiv., 194.1.

p-Thiocyanobenzoic Acid.—A diazotized solution of *p*-aminobenzoic acid was prepared by adding 17.5 g. (0.25 mole) of sodium nitrite in 70 cc. of water to a mixture of 34.0 g. (0.25 mole) of *p*-aminobenzoic acid, 50 ml. of concd. hydrochloric acid and 115 cc. of water cooled to 0–5°. This solution was added slowly to an ice-cold mixture containing 50 g. of potassium thiocyanate and a suspension of cuprous thiocyanate, which was prepared by slowly heating over the steam-bath a mixture of 40.0 g. (0.25 mole) of cupric sulfate, 50.0 g. (0.50 mole) of potassium thiocyanate and 100 ml. of water. The reaction mixture turned black during the addition. It was allowed to warm slowly to room temperature; when the evolution of nitrogen had ceased, it was placed on the steam-bath for 30 minutes. The resulting mixture was cooled, and extracted with 1.0 liter of ether in 10 portions. The ether extracts were combined and extracted with 200 ml. of a satd. sodium bicarbonate solution. Acidification of this extract gave a very fine yellow powder which consisted of *p*-thiocyanobenzoic acid and *p*-carboxyphenyl disulfide. This powder was boiled in one liter of water, and the insoluble disulfide was removed by filtration. Cooling the solution gave 10.1 g. (23%) of a white material, m.p. 208–210°. Recrystallization from benzene-hexane gave white leaflets, m.p. 209–210°.

Anal. Calcd. for $C_8H_5O_2SN$: C, 53.61; H, 2.81; neut. equiv., 179.2. Found: C, 53.80; H, 2.88; neut. equiv., 178.5.

S-Acetylmonothiohydroquinone.—Sixty grams of ice followed by 6.63 g. (0.065 mole) of acetic anhydride were added to a cold solution of 7.2 g. (0.057 mole) of monothiohydroquinone,[31] 2.4 g. (0.06 mole) of sodium hydroxide and 20 cc. of water. The solution was shaken for 10 minutes, acidified with acetic acid and extracted with 100 cc. of chloroform in 4 portions. The chloroform extracts were combined and dried over anhydrous sodium sulfate. Evaporation of the chloroform followed by crystallization of the residual oil from benzene–hexane gave 4.3 g. (44%) of long shiny white needles, m.p. 85–86°. This material gave a blue–brown color with ferric chloride solution.

Anal. Calcd. for $C_8H_8O_2S$: C, 57.12; H, 4.79. Found: C, 57.18; H, 4.76.

p-Thiocyanophenol.—A solution of 50.0 g. (0.31 mole) of bromine in 50 ml. of methanol previously saturated with sodium bromide was added dropwise over a 3-hour period to a well stirred suspension of 27.0 g. (0.28 mole) of phenol, 200 ml. of methanol saturated with sodium bromide and 80.0 g. (1.0 mole) of sodium thiocyanate. The solution was kept at 0–5° during the addition. It was allowed to warm to room temperature, then poured into 1.5 liters of ice-water. The material which separated was filtered and recrystallized from methanol–water to give 33.0 g. (79%) of a white crystalline material, m.p. 54–56°. An additional recrystallization from aqueous methanol, followed by a recrystallization from benzene–hexane, gave long white needles, m.p. 62–63°. A melting point of 60–62° has been reported.[32]

Phenyl Thiolacetate.—Acetylation of sodium thiophenolate with acetic anhydride by the Schotten–Baumann procedure gave 84% of a colorless oil, b.p. 89–90° at 7–8 mm., $n^{25}D$ 1.5681. A b.p. of 228–230° and an index of refraction, $n^{22}D$ 1.5706, have been reported.[33]

Thiocyanobenzene.—The pasty material obtained by the addition of 42 cc. (0.86 mole) of concd. sulfuric acid to an ice-cold solution of 40.0 g. (0.27 mole) of *p*-thiocyanoani-

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[28] L. Doub and J. M. Vandenbelt, This Journal, **69**, 2714 (1947).

[29] C. K. Ingold, ref. 15, p. 177; C. K. Ingold and J. A. Jessop, *J. Chem. Soc.*, 2357 (1929); 713 (1930).

[30] Microanalyses were carried out by Mrs. M. White, Miss J. Sorenson and Miss H. Beck. Melting points are uncorrected.

[31] Prepared by the method of E. Miller and R. R. Read, This Journal, **55**, 1224 (1933).

[32] N. N. Melnikow, S. I. Skjarenko and J. M. Tscherkassow, *J. Gen. Chem.* (*U.S.S.R.*), **9**, 1819 (1939); *Chem. Zentr.*, **111**, I, 1641 (1940).

[33] F. Taboury, *Ann. chim. phys.*, [8] **15**, 61 (1908).

line[33] in 250 ml. of ethanol was diazotized at 0° by the slow addition of 23.0 g. (0.32 mole) of sodium nitrite in 55 ml. of water. The resulting light suspension was stirred an additional 40 minutes, then warmed slowly on the steam-bath until a steady evolution of nitrogen became apparent. After one hour the evolution of nitrogen ceased and the reaction mixture was steam distilled. The two liters of distillate which were collected were saturated with sodium chloride and extracted with 500 cc. of ether. Drying of the ether extracts followed by distillation of the ether gave a yellowish residue which was fractionated to yield 22.5 g. (62%) of a colorless oil, b.p. 93–95° at 8–9 mm. Redistillation gave a material, b.p. 89–90° at 8 mm., $n^{25}D$ 1.5712. A boiling point of 231–232° has been recorded.[34]

Anal. Calcd. for C_7H_5SN: N, 10.36. Found: N, 10.47.

Acidity Constant Measurements.—Ionization constants were determined with a Beckman model G *p*H meter standardized with Beckman buffers No. 14044, 3581 and 14049. The procedure used to measure the acidities of the substituted phenols in water, the substituted thiophenols in 48% by volume ethanol and the substituted benzoic acids in 50% ethanol has been described previously.[3–5] The numerical values are summarized in Tables V, VI and VII.

TABLE V

ACIDITY CONSTANTS OF SUBSTITUTED BENZOIC ACIDS IN 50% ETHANOL (BY VOLUME) AT 25°

Substituents	Concentration, mole/liter C^a	C_b	*p*H	pK_a	pK_a average
m-CH_3COO–	0.01750	0.00394	4.62	5.15	
	.01899	.00788	5.01	5.16	
	.01863	.01182	5.40	5.16	5.16
p-CH_3COO–	.01844	.00394	4.73	5.30	
	.01140	.00493	5.17	5.29	
	.01884	.01182	5.51	5.28	5.29
m-CH_3COS–	.01309	.00296	4.64	5.17	
	.01250	.00493	4.99	5.18	
	.01301	.00788	5.36	5.17	5.17
p-CH_3COS–	.01243	.00296	4.59	5.10	
	.01183	.00493	4.94	5.09	
	.01252	.00985	5.65	5.08	5.09
m-CH_3CONH–	.01713	.00394	4.83	5.35	
	.01855	.00788	5.23	5.36	
	.01851	.01182	5.59	5.34	5.35
p-CH_3CONH	.01710	.00394	5.17	5.69	
	.01594	.00640	5.53	5.68	
	.01627	.00985	5.86	5.67	5.68
p-SCN	.02644	.01562	5.12	4.96	
	.02413	.00735	4.62	4.98	
	.02291	.00459	4.37	4.97	4.97

[a] *C* denotes the stoichiometric concentration of the acid under measurement and C_b the amount of sodium hydroxide added, which was taken as the concentration of anion.

Ultraviolet Absorption Spectra.—The ultraviolet absorption spectra of thiocyanobenzene and phenyl thioacetate were taken in water. Those of *p*-thiocyano- and *p*-thioacetoxyphenols were taken in water and in 0.10 *N* sodium hydroxide. The spectra were taken with a Cary recording spectrophotometer equipped with a hydrogen discharge tube, 1-cm. quartz cells and thermostated cell holders. The temperatures of the solutions were maintained at 28 ± 1° and the spectra were recorded from 205 to 400 mμ. Each sample was weighed and processed by a method previously described.[4]

Competitive Aromatic Substitution Reactions.—A number of experiments of this type were run. The nitration of a thiocyanobenzene–benzene mixture with acetyl nitrate is typical of these. The others for which the results are reported are of a similar type.

TABLE VI

ACIDITY CONSTANTS OF SUBSTITUTED PHENOLS IN WATER AT 25°

Substituents	Concentraton, mole/liter *C*	C_b	*p*H	pK_a	pK_a average
m-CH_3S–	0.01830	0.00344	8.79	9.42	
	.02020	.00860	9.30	9.43	
	.02299	.01378	9.59	9.41	9.42[a]
p-CH_3S–	.01619	.00344	8.91	9.48	
	.01711	.00689	9.30	9.46	
	.01654	.01033	9.69	9.47	9.47[a]
m-$(CH_3)_2N$–	.00961	.00394	9.68	9.84	
	.00968	.00591	10.00	9.83	
	.00475	.00236	9.86	9.86	
	.00722	.00148	9.26	9.85	9.85
p-$(CH_3)_2N$–	.00698	.00333	10.15	10.22	
	.01281	.00587	10.14	10.23	
	.01289	.00636	10.16	10.21	10.22
p-CH_3COS	.01524	.00493	8.56	8.88	
	.01266	.00591	8.82	8.87	
	.01243	.00690	8.96	8.89	8.88
p-SCN–	.01929	.00641	8.26	8.56	
	.01981	.00919	8.52	8.58	
	.02229	.01323	8.73	8.57	8.57

[a] The pK_a of both *m*-CH_3S and *p*-CH_3S have been reported[3a] as 9.53. The σ values for these groups given in Table I were calculated on the basis of the pK_a values given here using $\rho = 2.29$, and $\log K_0 = -9.95$.[4]

TABLE VII

ACIDITY CONSTANTS OF SUBSTITUTED THIOPHENOLS IN 48% ETHANOL (BY VOLUME) AT 25°

Substituents	Concentration, mole/liter *C*	C_b	*p*H	pK_1	pK_1 average
m-$(CH_3)_2N$–	0.01474	0.00378	7.47	7.93	
	.01575	.00640	7.78	7.94	
	.01732	.01035	8.12	7.95	7.94
p-$(CH_3)_2N$–	.02093	.00394	7.74	8.38	
	.02072	.00788	8.16	8.37	
	.02037	.01182	8.51	8.37	8.37

Nitration of a Thiocyanobenzene–Benzene Mixture.—A solution of 3.16 ml. (0.05 mole) of concd. nitric acid (15.8 *N* against standard sodium hydroxide solution), and 10 ml. of acetic anhydride was added slowly to a solution of 3.90 g. (0.05 mole) of benzene and 6.75 g. (0.05 mole) of thiocyanobenzene. The reaction mixture which was kept at 0–5° during the addition was raised to 20–25° and allowed to stand 15 hours. The solution was poured on 100 g. of ice and, after hydrolysis of the acetic anhydride, was extracted with 250 ml. of ether in 5 portions. The ether extracts were combined, and after evaporation of the ether the residue obtained was kept on the steam-bath at 60° with 20 ml. of 20% sodium hydroxide to hydrolyze the thiocyano group. The reaction mixture was steam distilled until the distillate became clear. The liquid collected, 110 ml., was extracted with ether and the ether extract dried over calcium chloride. Evaporation of the ether followed by distillation of the residue gave 4.82 g. (80%) of a liquid, b.p. 207–209°, $n^{25}D$ 1.5525 which agreed in properties with nitrobenzene, b.p. 210.9°, $n^{22}D$ 1.55297°.[35] An infrared analysis confirmed its identity. The residue from the steam distillation was neutralized with concd. hydrochloric acid and oxidized with ferric chloride (to convert any mercaptan present to disulfide). The mixture was extracted with ether, the ether extracts were combined and dried and the ether was distilled. The residue obtained was recrystallized from 50% aqueous ethanol to give 4.5 g. (0.0205 mole) of a white material, m.p. 58–60°, which did not depress the melting point of an authentic sample of phenyl disulfide. As two moles of thiocyanobenzene correspond to one mole of phenyl disulfide,

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(34) O. Billeter, *Ber.*, **7**, 1754 (1874).

(35) I. M. Heilbron, "Dictionary of Organic Compounds," Oxford Univ. Press, New York, N. Y., 1938, Vol. 3.

the unreacted thiocyanobenzene recovered in the form of phenyl disulfide was 0.041 mole (82%).

Results of Other Competitive Experiments.—*Nitration of thiocyanobenzene–benzene with nitric acid–sulfuric acid:* 94% yield of nitrobenzene. *Nitration of acetanilide–benzene with nitric acid in acetic acid:* 55% yield of *p*-nitroacetanilide and 24% recovery of acetanilide. *Nitration of acetanilide-benzene with sulfuric acid–nitric acid:* 57% yield of nitrobenzene and 70% recovery of impure acetanilide. *Bromination of acetanilide-benzene:* 91% yield of *p*-bromoacetanilide.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF MARYLAND]

A Comparison of Raney Nickel and Raney Cobalt Catalysts for the Hydrogenation of Oximes

BY WILKINS REEVE AND JACK CHRISTIAN

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A comparison of Raney cobalt and Raney nickel catalysts for the hydrogenation of six oximes has been made. Raney cobalt generally produced primary amines of as high purity and yield as did Raney nickel. In some cases, Raney cobalt produces best results in ethanol or dioxane solvent without addition of ammonia, whereas Raney nickel often requires an ammoniacal solvent for best results. With both catalysts, both the solvent and the presence or absence of ammonia have an important bearing on the yield and purity of the primary amine obtained.

The use of nickel as a catalyst for the hydrogenation of oximes and nitriles was introduced by Sabatier and his students in 1905.[1] They also used a cobalt catalyst for the hydrogenation of olefins, acetylene, benzene and some carbonyl compounds, but found its catalytic properties to be inferior to those of nickel.[2] Raney cobalt was prepared by Faucounau[3] and used as a hydrogenation catalyst, but the hydrogenation of oximes was not studied. Schmidt in Germany, and later workers, demonstrated cobalt catalysts to be excellent for the hydrogenation of nitriles and dinitriles.[4] Since powdered Raney cobalt alloy containing 40% cobalt and 60% aluminum is now commercially available, it seemed desirable to examine the use of Raney cobalt as a hydrogenation catalyst for oximes with the object of determining its merits relative to Raney nickel.

Six oximes have been hydrogenated over Raney cobalt and Raney nickel under comparable conditions. With three of the oximes, ethanol with and without added anhydrous ammonia, and dioxane likewise with and without ammonia, were employed as solvents, so that comparisons could be made under four different conditions. With the other three oximes, the Raney nickel was used with ammoniacal ethanol solvent and the Raney cobalt with ethanol and dioxane without ammonia. In all cases, the amines obtained were analyzed for secondary plus tertiary amine content by titrating with acid in the presence of salicylaldehyde, and for primary amine content by titrating with acid and making the necessary correction for non-primary amine content.[5] The results are summarized in Table I.

Raney nickel has long been known to be an excellent catalyst for the hydrogenation of oximes.[6]

TABLE I

HYDROGENATION OF OXIMES OVER RANEY NICKEL AND RANEY COBALT[a]

Catalyst	Solvent	Yield, %	B.p. °C.	B.p. Mm.	Amine, % Primary	Amine, % Sec. and tert.
	n-$C_3H_7CH:NOH$[b]					
Co	Ethanol	95	78–81	760	97	5
Ni	Ethanol	92	79–84	760	82	5
Co	Ethanol with 3% NH_3	86	79–85	760	96	5
Ni	Ethanol with 3% NH_3	97	79–83	760	95	5
Co	Dioxane	86	79–85	760	96	1
Ni	Dioxane	87	79–83	760	91	11
Co	Dioxane with 1.2% NH_3	92	79–86	760	89	15
Ni	Dioxane with 1.2% NH_3	96	79–83	760	94	6
	$C_6H_5CH:NOH$[b,c,e]					
Co	Ethanol	84	89–91	15	96	2
Ni	Ethanol	76	179–183	760	96	1
Co	Ethanol with 3% NH_3	91	89–98	15	97	0
Ni	Ethanol with 3% NH_3	81	90	20	98	0
Co	Dioxane	78	177–181	760	96	0
Ni	Dioxane	88	90	15–20	99	0
Co	Dioxane with 1.2% NH_3	89	182–186	760	96	0
Ni	Dioxane with 1.2% NH_3	68	181–183	760	97	1
	2-Furaldoxime[b,c]					
Co	Ethanol	39	63–67	30	96	1
Ni	Ethanol with 3% NH_3	51	145–150	760	96	1
Co	Dioxane	43	147–151	760	97	1
	$C_2H_5(CH_3)C:NOH$[b,c]					
Co	Ethanol	93	65–68	760	97	2
Ni	Ethanol with 3% NH_3	92	65–68	760	95	3
Co	Dioxane	96	64–68	760	97	4
	t-$C_4H_9(CH_3)C:NOH$[d]					
Co	Ethanol	59	103–105	760	97	0
Ni	Ethanol with 3% NH_3	63	103–106	760	99	0
Co	Dioxane	50	102–105	760	99	0
	$C_6H_5(CH_3)C:NOH$[c,e]					
Co	Ethanol	91	182–188	760	83	4
Ni	Ethanol	88	79–80	21	93	3
Co	Ethanol with 3% NH_3	86	185–189	760	90	3
Ni	Ethanol with 3% NH_3	86	185-189	760	95	2
Co	Dioxane	87	179–189	760	80	3
Ni	Dioxane	95	74–78	10	96	2
Co	Dioxane with 1.2% NH_3	87	185–186	760	96	1
Ni	Dioxane with 1.2% NH_3	75	183–186	760	94	2

[a] All hydrogenations were carried out in a 300-ml. steel reaction vessel under an initial hydrogen pressure of 200–220 atm. with 0.25 teaspoon (about 2 g.) of the Raney catalyst and 25 or 30 g. of the oxime dissolved in 100 ml. of solvent. The reaction temperature was chosen so that the hydrogenation was substantially complete in 10 to 30

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[1] A. Mailhe, *Compt. rend.*, **140**, 1691 (1905); P. Sabatier and J. B. Senderens, *ibid.*, **140**, 482 (1905).

[2] P. Sabatier and J. B. Senderens, *Ann. chim. phys.*, [8], **4**, 344 (1905).

[3] L. Faucounau, *Bull. soc. chim. France*, [5] **4**, 63 (1937).

[4] See ref. 1 of W. Reeve and W. M. Eareckson, THIS JOURNAL, **72**, 3299 (1950), for leading references.

[5] S. Siggia, J. G. Hanna and I. R. Kervenski, *Anal. Chem.*, **22**, 1295 (1950).

[6] H. Adkins, "Reactions of Hydrogen," University of Wisconsin Press, Madison, Wisconsin, 1937.